

drying, low odor, easy cleaning, great durability, and impermeability to dirt. Latex paints have as their major film-forming constituent a synthetic resin latex, with or without other film-forming constituents added, in an oil-water emulsion-type system. The continuous phase consists of an alkali-dispersed hydrophilic colloid in water and contains two or more different types of particles in suspension.

Styrene-butadiene rubber (SBR) copolymer was the original quality film-former in latex paint. Polyvinyl acetate (PVA), acrylics, and PVA-acrylic copolymers have largely replaced SBR as film formers in today's trade. Quality is substantially improved.

Proper paint formulation centers around the specific requirements of the particular application. These requirements are hiding power, color, weather resistance, washability, gloss, metal anticorrosive properties, and consistency, as related to type of application (brushing, dipping, spraying, or roller coating). Individual requirements are met by proper choice of pigments, extenders, and vehicles by the paint formulator. Since the techniques of paint technology formulation are still largely empirical, it is difficult to predict the properties of a specific formulation, and this often means that a considerable number of trials have to be run before the desired properties are obtained. However, by using simple statistical methods, it has been demonstrated that more efficient testing and development results are obtainable. Almost all the major paintmakers have developed some type of automated color-control system; new methods reduce the time required to match paint and, by giving closer control of pigment requirements, keep production costs down.³

For the modern paint formulator, some authorities believe the most important concept is that of pigment volume concentration (PVC). It is defined as:

$$\text{PVC} = \frac{\text{volume of pigment in paint}}{\text{volume of pigment in paint} + \text{volume of nonvolatile vehicle constituents in paint}}$$

The PVC largely controls such factors as gloss, reflectance, rheological properties, washability, and durability. The inherent vehicle requirements of the pigment-extender combination being applied, however, affect the PVC used in a given formulation. As a consequence there is usually a range of PVC for a given paint, as indicated in the following tabulation:

Flat paints	50-75%	Exterior house paints	28-36%
Semigloss paints	35-45%	Metal primers	25-40%
Gloss paints	25-35%	Wood primers	35-40%

The PVC of a given formulation serves as the guide for reformulation work, using different pigment or vehicle combinations, and as such is extremely useful to the paint formulator. The addition of pigment continues to reinforce and improve the film-forming properties until a critical concentration (CPVC) is reached. At this point and beyond, the resistance properties of the paint decrease, as the film becomes porous, causing the paint to weather faster and lose abrasion resistance and flexibility.⁴

MANUFACTURING PROCEDURES. The various operations needed to mix paints are wholly physical. These unit operations are shown in proper sequence in the flowchart in Fig. 8.1

³Color Technology, *Chem. Eng.* 75 (17) 146 (1968).

⁴Weismantel, Paints and Coatings for CPI Plants and Equipment, *Chem. Eng.* 88 (8) 130 (1981); Rowland, Graphical Solution to CPVC Problems in Latex Paints, *J. Coat. Technol.* 54 (686) 51 (1982).

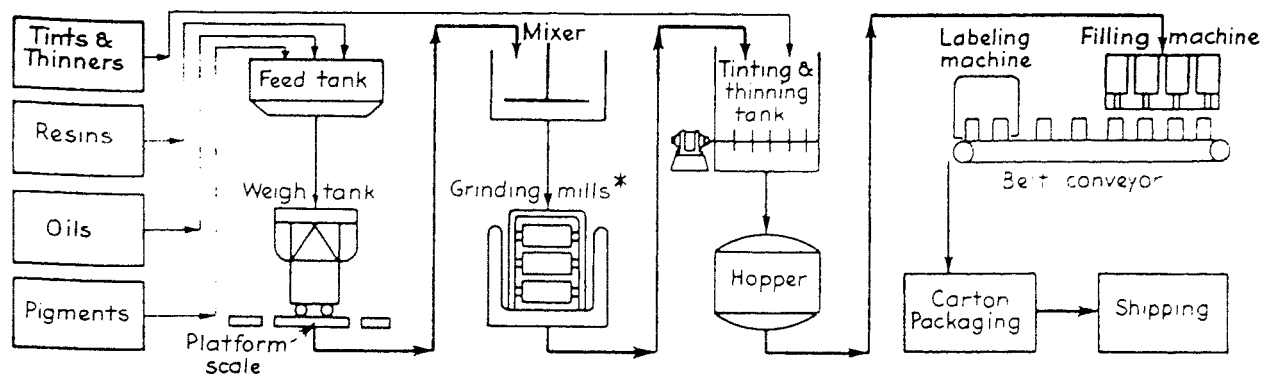


Fig. 8.1. Flowchart for the mixing of paint. **NOTE:** Because a complete paint factory consumes upward of 2000 different raw materials and produces ten times as many finished products, it is not possible to give yields, etc.

*Many types of grinding mills are used in the same plant, either in series or in parallel. Some of them are ball mills, high-speed dispersers, and three- and five-roll steel mills

Chemical conversions are involved in the manufacture of the constituents of paints as well as in the drying of the film. The manufacturing procedures illustrated are for a mass-production paint. The weighing, assembling, and mixing of the pigments and vehicles take place on the top floor. The mixer may be similar to a large dough kneader with sigma blades. The batch masses are conveyed to the floor below, where grinding and further mixing take place. A variety of grinding mills may be used. One of the oldest methods is grinding, or dispersion, between two buhrstones; however, ball-and-pebble mills and steel roller mills were the principal grinding mills used until recently. Sand mills, high-speed agitators, and high-speed stone mills are being used increasingly to grind paint and enamels. The types of pigments and vehicles are dominant factors in the choice of equipment used (Figs. 8.2 and 8.3).

The mixing and grinding of pigments in oil require much skill and experience to secure a smooth product without too high a cost. Perry⁵ presents these operations in a useful manner, with pictures of various mills and tabulations of the engineering factors concerned. No one machine is universally applicable.

After mixing, the paint is transferred to the next-lower floor, where it is thinned and tinted in agitated tanks, which may hold batches of several thousand liters. The liquid paint is strained into a transfer tank or directly into the hopper of the filling machine on the floor below. Centrifuges, screens, or pressure filters are used to remove nondispersed pigments. The paint is poured into cans or drums, labeled, packed, and moved to storage, each step being completely automatic.

For latex paints, the dispersant and ammonia are added to water in a pony mixer, followed by pigments premixed and ground in a ball mill. The pigments and extenders most used are water-dispersible grades of titanium dioxide, zinc sulfide, lithopone, and regular grades of barium sulfate, mica, diatomaceous silica, clay, and magnesium silicate. A combination of four or five inerts is generally employed. The usual colored pigments may be used for tinting, with certain exceptions such as prussian blue, chrome yellow, chrome green, and carbon black. The first three are sensitive to alkalis, and the last tends to break the emulsion. Also, sodium-free alkalis and pigments are preferred, since they minimize efflorescence caused by sodium sulfate on the paint surface. Interior pigments must, by law, be nonpoisonous if

⁵Perry, 5th ed., p. 8-42 for roller mill and pigment grinding, p. 19-24 for kneaders, p. 5-25 for ball mills, and p. 8-8 for principles of size reduction.

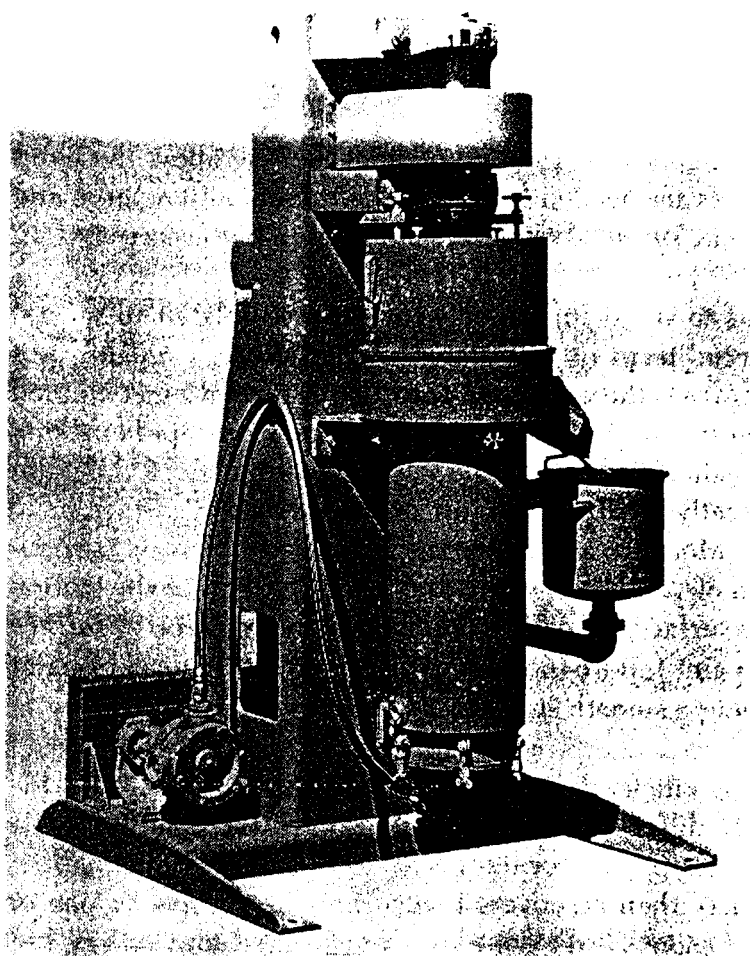


Fig. 8.2. A sand-grinding mill, illustrating the process and apparatus developed by DuPont. This mill is a combination type, with round grains of Ottawa sand which grind and disperse the pigments in the medium grinding chamber, followed by a screen which holds back the sand.

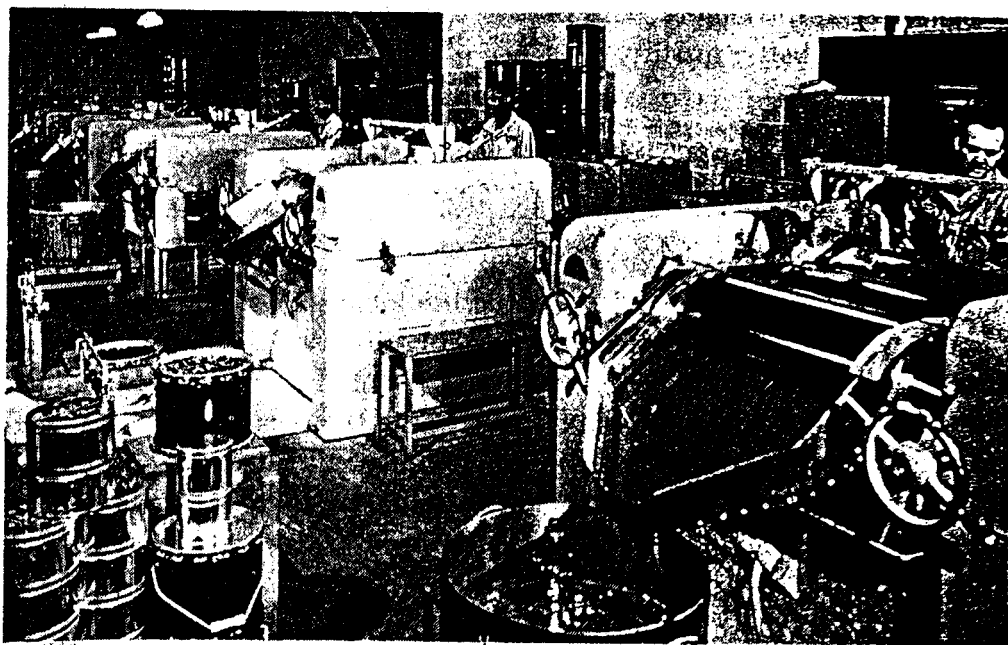


Fig. 24.3. Three-roll mill. (J. H. Day Co.)

ingested. The film formers are added to the pigment dispersion, followed by a preservative solution (usually chlorinated phenols) and an antifoam (sulfonated tallow or pine oil). The latex emulsion is stirred in slowly, followed by water. The paint is mixed, screened, and mixed again before packaging. A typical paint consists of 35% pigment and filler and about 21% film-forming ingredients. Latex paints require the addition of thickeners to allow the paint to be spread satisfactorily. Other additives are needed for specific purposes: antibacterial and antimildew agents, freeze-thaw stabilizers, surfactants, defoamers, and pH adjusters.

PAINT FAILURE. The failure of paints to stand up under wear may be related to several causes, and in each case there is a special term used to describe the failure. *Chalking* is a progressive powdering of the paint film from the surface inward that is caused by continued and destructive oxidation of the oil after the original drying of the paint. Very rapid chalking is termed *erosion*. *Flaking*, sometimes called *peeling*, is due to poor attachment of the paint to the surface being covered and is usually attributed to dirt or grease on the surface or to water entering from behind the paint. Moisture accumulation underneath paint is particularly destructive. *Alligatoring* is a form of peeling in which the center portion of the section starting to peel remains attached to the surface. *Checking* denotes a very fine type of surface cracking. As opposed to these types of paint failure, normal wear is gradual removal of paint from the surface by the elements, leaving a smooth surface.

PAINT APPLICATION. A surface that is efficiently painted, varnished, or lacquered often requires the application of a number of different coatings varied to suit the condition. For example, most surfaces require the use of a primer, or filler coat, to smooth over inequalities and to secure better adherence. This may then be covered with the paint proper in one or more applications. Much application of paint is still done by hand brushes and rollers, but dipping and spray painting are gaining favor because of the ease and rapidity of spread, thus saving labor, though wasting a little material. The use of electric charges greatly reduces spray paint loss. A wide variety of atomizers for spraying is available, including internal mixing and the more common external mixing. Spray guns are operated frequently at pressure of 275 to 414 kPa. Coating materials in aerosol containers, sold in millions, are popular because of their convenience of application. Prefinishing of metal and wood sheets is done by reverse or direct roll coating at the factory. This process is more economical than painting on the job, and the finishes are of better quality.

PIGMENTS⁶

Pigments⁷ (Table 8.3) are colored, organic and inorganic insoluble substances used widely in surface coatings, but they are also employed in the ink, plastic, rubber, ceramic, paper, and linoleum industries to impart color. A large number of pigments and dyes are consumed because different products require a particular choice of material to give maximum coverage, economy, opacity, color, durability, and desired reflectance. White lead, zinc oxide, and lithopone were once the principal white pigments; colored pigments consisted of prussian blue.

⁶ECT, 3d ed., vol. 17, 1982, pp. 788–889; Patton, *Pigment Handbook*, Wiley, New York, 1973.

⁷Specifications for pigments, ASTM Standards, vol. 8, 1989.

Table 8.3 Pigments and Extenders for Surface Coatings

Ingredients		Function
Pigments		
White hiding pigments	Yellow pigments	To protect the film by reflecting the destructive ultraviolet light, to strengthen the film, and to impart an aesthetic appeal. Pigments should possess the following properties: opacity and good covering power, wettability by oil, chemical inertness, nontoxicity or low toxicity, reasonable cost
Titanium dioxide	Litharge	
Zinc oxide	Ocher	
Lithopone	Lead or zinc chromate	
Zinc sulfide	Hansa yellows	
Antimony oxide	Ferrite yellows	
Black pigments	Cadmium lithopone	
Carbon black	Orange pigments	
Lampblack	Basic lead chromate	
Graphite	Cadmium orange	
Iron black	Molybdenum orange	
Blue pigments	Green pigments	
Ultramarine	Chromium oxide	
Copper phthalocyanine	Chrome green	
Iron blues	Hydrated chromium oxide	
Red pigments	Phthalocyanine green	
Red lead	Permanganate greens (phthalocyanine blue plus zinc chromate)	
Iron oxides	Brown pigments	
Cadmium reds	Burnt sienna	
Toners and lakes	Burnt umber	
Metallics	Vandyke brown	
Aluminum	Metal protective pigments	
Zinc dust	Red lead	
Bronze powder	Blue lead	
	Zinc, basic lead, and barium potassium chromates	
Extenders or Inerts		
China clay	Gypsum	To reduce the pigment cost and in many cases to increase the covering and weathering power of pigments by complementing pigment particle size, thus improving consistency, leveling, and settling
Talc	Mica	
Asbestos (short fibers)	Barite, barium sulfate	
Silica and silicates	Blanc fixe	
Whiting		
Metal stearates		

lead chromates, various iron oxides, and a few lake colors. Today titanium oxide in many varieties is almost the only white pigment used. Lead pigments, formerly of major importance, are now prohibited by law for many uses.

White Pigments

The oldest and formerly most important of the white pigments is white lead, which is no longer permitted as a constituent of most paints. Zinc oxide, another white pigment formerly widely used, is now of only minor importance. Table 8.4 presents a summary of the characteristics of white pigments.

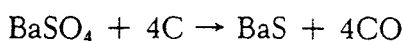
LITHOPONE. Lithopone is a mixed zinc sulfide–barium sulfate pigment that contains about 30% zinc sulfide. The original light sensitiveness has been overcome by raw material purification and by the addition of such agents as polythionates and cobalt sulfate. Lithopone is a

Table 8.4 Comparison of White Pigments

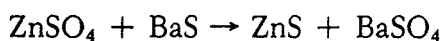
	Titanium Dioxide		Zinc Oxide	White Lead Basic Lead Carbonate
	Anatase	Rutile		
Refractive index	2.55	2.70	2.08	2.0
Average particle size, μm	0.2	0.2–0.3	0.2–0.35	1.0
Density, g/cm^3	3.8–4.1	3.9–4.2	5.6	7.8–6.9
Oil absorption, grams of oil/100 g pigment	18–30	16–48	10–25	11–25
Relative hiding power	100	125–135	20	15
Price (1981), \$ per kilogram	1.51	1.65	1.03	1.54

brilliantly white, extremely fine, cheap, white pigment. It is particularly well adapted to interior coatings.

The manufacture is shown diagrammatically in Fig. 8.4 where the barium, zinc, and lithopone circuits are represented by different types of lines. The barium sulfide solution is prepared by reducing barite ore (BaSO_4) with carbon and leaching the resulting mass. The equation is:

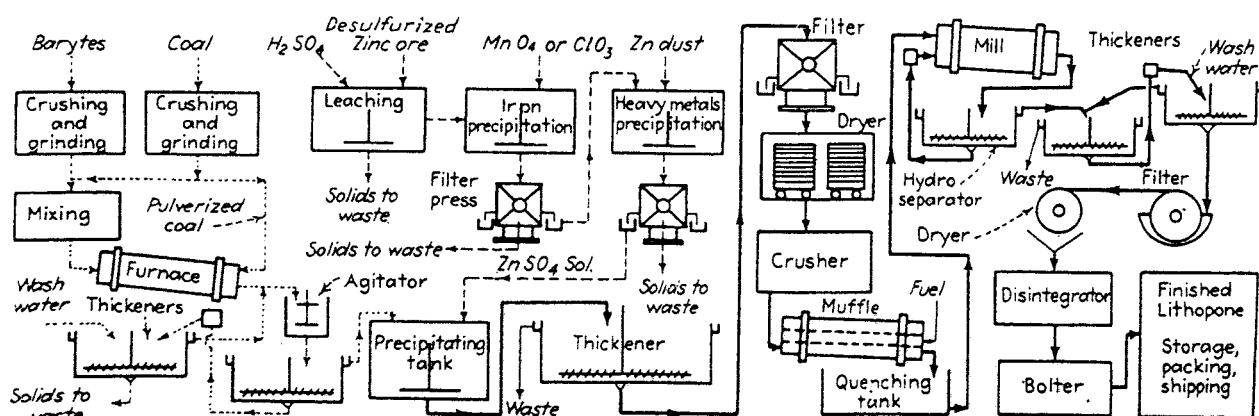


Scrap zinc or concentrated zinc ores are dissolved in sulfuric acid, and the solution purified as shown. The two solutions are reacted, and a heavy mixed precipitate results which is 28 to 30% zinc sulfide and 72 to 70% barium sulfate.



This precipitate is not suitable for a pigment until it is filtered, dried, crushed, heated to a high temperature, and quenched in cold water. The second heating in a muffle furnace at 725°C produces crystals of the right optical size.

Lithopones are used in water-based paints because of their excellent alkali resistance. They



In order to produce 1 t of lithopone, the following materials and utilities are needed:

Barytes	0.85 t	Zinc ore (60% zinc)	0.4 t
Coal (half for steam)	1.1 t	H_2SO_4 (50°Bé)	0.5 t
Electricity	400 MJ	Direct labor	15 work-h

Fig. 8.4. Flowchart for lithopone manufacture. - - - - - indicates the barium circuit, the zinc circuit, and ——— the lithopone circuit.

are also used as a whitener and reinforcing agent for rubber and as a filler and whitener for paper.

TITANIUM DIOXIDE. The most important white pigment is TiO_2 . It is marketed in two crystalline forms, anatase and the more stable rutile. Almost all the TiO_2 used in paints is the rutile form. Anatase can be converted to rutile by heating to 700 to 950°C. TiO_2 is widely employed in exterior paints and also in enamels and lacquers. A typical exterior white paint contains about 60% pigment, of which 20% is TiO_2 , 60% talc, and 20% mica. Such a formulation has long life through controlled chalking (a layer of loose pigment powder on the surface of the paint film, which acts as a self-cleaner for the paint) and presents a good surface for subsequent repainting. About 50 percent of this pigment is consumed in paints, varnishes, and lacquers and the second most important customer (23 percent) is the paper industry. Another important use is in the coloring of plastics. Demand in 1981 was 750,000 t.^{8,8a}

The two important methods for producing TiO_2 are the sulfate and chloride processes. The sulfate is the older process, but the chloride process has largely supplanted it and produces over 60 percent of the U.S. production. The sulfate process uses the cheaper, domestic ore, ilmenite, as a raw material, while the chloride process requires the more expensive imported ore, rutile. Ilmenite can be converted to synthetic rutile, and DuPont has a patented chloride process that uses ilmenite.

The sulfate process has traditionally used batch ore digestion in which concentrated sulfuric acid is reacted with ilmenite. This reaction is very violent and causes the entrainment of SO_x and H_2SO_4 in large amounts of water vapor; they are subsequently emitted to the atmosphere in far larger quantities than are allowed by clean air standards. In an effort to reduce the particulate emissions, scrubbers have been installed at most plants, but these, in turn, have necessitated the treatment of large quantities of scrubbing liquid before discharge. Other waste-disposal problem products are spent sulfuric acid and copperas ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$).

The chloride process utilizes the treatment of rutile (natural or synthetic) with chlorine gas and coke to produce titanium tetrachloride. The titanium tetrachloride is distilled to remove impurities and then reacted with oxygen or air in a flame at about 1500°C to produce chlorine and very fine-particle titanium dioxide. The chlorine is recycled (Fig. 8.5). The waste products are easier to dispose of than those formed by the sulfate process.

A new sulfate process that claims to eliminate many of the old pollution problems has been introduced by NL Industries.⁹ This is a continuous process using relatively dilute sulfuric acid

⁸Chem. Week 130 (26) 43 (1982).

^{8a}t = 1000 kg.

⁹Kaplan, Improved Titanium Dioxide Process Keeps Plant Alive, *Chem. Eng.* 89 (12) 86 (1982).

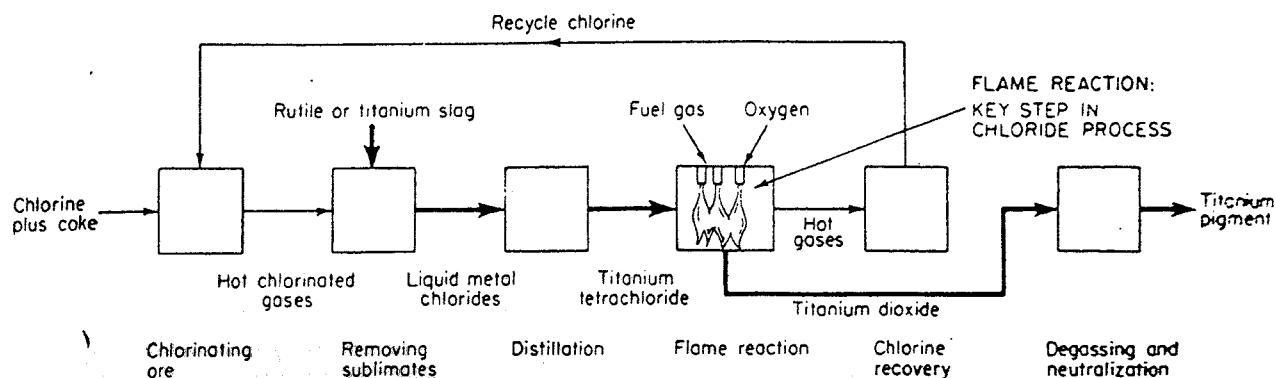
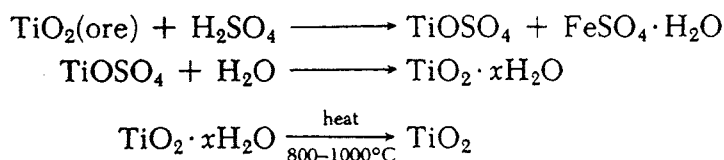


Fig. 8.5. Titanium dioxide manufacture by the chloride process.

(25 to 60%) to temper the violent, original reaction and reduce the amount of water-vapor-entrained particulates. As the process uses more dilute acid than the older batch process, more of the spent acid can be recycled. Flow diagrams for both the batch and continuous processes are shown in Fig. 24.6.



The hydrolysis reaction is dependent upon many factors: quantity and quality of the seeds added to the colloidal suspension of TiO_2 , concentration, rate of heating, and pH. Introduction of seeds prior to hydrolysis ensures production of the desired form. Using anatase seeds, 6 h of boiling is needed, and with rutile seeds, the time can be shortened to 3 h.

BARIUM SULFATE. Barium sulfate, often prepared by grinding the ore barite, is not usually used alone as a white pigment because of its poor covering power, but is widely used as a pigment extender. It also contributes to gloss. Its principal use (over 90 percent) is in oil-drilling muds. Only 3 percent of U.S. production is used in paints. Blanc fixe is made by precipitation of a soluble barium compound, such as barium sulfide or barium chloride, by a sulfate. This form has finer particles than the ground barite and is often used in printing inks to impart transparency.

Black Pigments

The only major black pigments are the carbon blacks. These come in various shades and their manufacture is discussed under industrial carbon in Chap. 8. Lampblack, which has a larger particle size, is used for tinting to produce shades of gray. The carbon blacks are very opaque and have excellent durability, resistance to all types of chemicals, and lightfastness. They

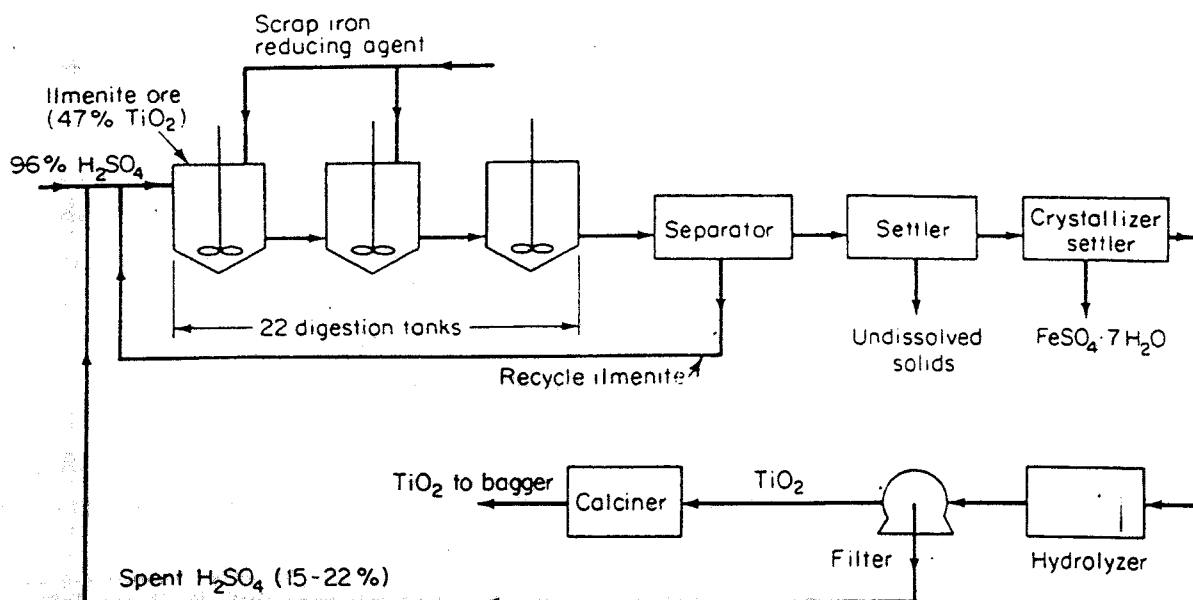


Fig. 8 .6. Titanium dioxide manufacture by two types of sulfuric acid processes.

should not be used in direct contact with iron and steel in primer coatings because they stimulate metal corrosion.

Blue Pigments

ULTRAMARINE BLUE. This is a complex sodium aluminum silicate and sulfide made synthetically. Because it has a sulfide composition, it should not be used on iron or mixed with lead pigments. Ultramarine is widely used as bluing in laundering to neutralize the yellowish tone in cotton and linen fabrics. It is also applied for whitening paper and other products. Special grades, low in free sulfur, are used in inks.

PHTHALOCYANINE BLUES. This group of blues, marketed in the United States since 1936, is particularly useful for nitrocellulose lacquers in low concentrations as a pigment highly resistant to alkalis, acids, and color change. For details of manufacture, see Chap. 39. As presently produced, they are most stable pigments, resistant to crystallization in organic solvents, and essentially free from flocculation in coatings. Both the greens and the blues have high tinting power and are used in latex paints and in printing inks, as well as all types of interior and exterior coatings. They are prepared by reacting phthalic anhydride with a copper salt with or without ammonia.¹⁰

FERROCYANIDE BLUES. These blues are known as prussian blue, chinese blue, milori blue, bronze blue, antwerp blue, and Turnbull's blue. As these names have lost much of their original differentiation, the more general term *iron blues* is preferred. These pigments are made in essentially the same manner by the precipitation of ferrous sulfate solutions (sometimes in the presence of ammonium sulfate) with sodium ferrocyanide, giving a white ferrous ferrocyanide, which is then oxidized to ferric ferrocyanide, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$, or to $\text{Fe}(\text{NH}_4)[\text{Fe}(\text{CN})_6]$ by different reagents such as potassium chlorate, bleaching powder, and potassium dichromate. The pigment is washed and allowed to settle, since filtration is extremely difficult because of its colloidal nature. Iron blues possess very high tinting strength and good color performance; their relative transparency is an advantage in dip-coating foils and bright metal objects, and for colored granules for asphalt shingles. They cannot be used in water-based paints because of their poor alkali resistance.

Red Pigments

RED LEAD. Red lead (Pb_3O_4) has a brilliant red-orange color, is quite resistant to light, and finds extensive use as a priming coat for structural steel because it possesses corrosion-inhibiting properties. Red lead, or minium, is manufactured by the *regular process* by oxidizing lead to litharge (PbO) in air and further oxidizing the litharge to red lead. In the *fumed process*, which produces smaller particles, molten lead is atomized by compressed air and then forced through the center of a gas flame, which in turn converts it into litharge as a fume collected in filter bags. The litharge is then oxidized to red lead by roasting in air.

FERRIC OXIDE (Fe_2O_3). This is another red pigment employed in paints and primers, as well as in rubber formulation. A wide range of natural red oxide pigments is available and, because

¹⁰Tech. Bull. 902, Am. Cyanamid Co.